

# Studying the Tribological and Mechanical Properties of the PMMA Nano Composite Coating

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## Abstract

This work includes preparing and studying a transparency polymeric coating that has good tribological and mechanical properties. Coating enhanced with nanoparticles can absorb UV radiation while keeping transparency. Also, coating leads to lowering the friction coefficient that improves the coating's wear resistance performance for mobile and computer screen applications, also it leads to increasing the life span of car lamp covers and glass, plastic windows and coating of solar cells. The nanocomposite coating consists of Graphene oxide (GO), Graphene oxide modified (MGO). Composite coating samples with GO and MGO nanoparticles at various weight percentages (0, 0.25, 0.5, and 1 wt%) were created by employing a solution mixing process. Scanning electron microscopy (SEM) was used to evaluate the distribution of nano and fracture failure. Hardness, DSC, wear and scratch tests were done. Additionally, the relationship between tribological and mechanical behavior was studied, as well as the mechanical properties of PMMA nanocomposites coating with the nanoparticle addition. The results showed that adding GO, MGO nanoparticles enhanced the PMMA's tribological performance. It was discovered that PMMA nanocomposites coating had a lower wear and friction coefficient than pure PMMA coating. According to the microstructure data, the ultrasonic treatment significantly contributed to the nanoparticles' good dispersion and decreased agglomeration. The results of mechanical qualities, such as hardness, demonstrated a discernible improvement..

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**Keywords:** PMMA; GO; Nanocomposite; Coating; Modified Graphene oxide..

## 1. Introduction

Organic coatings are used in coating technology to provide surface protection, ornamental finishes, and a number of additional functions for products and trade. Many everyday goods are only usable and hence marketable because of their surface treatment A polymer is a high-molecular-weight molecule made up of a large number of structural units linked together by chemical bonds [1].

Nano-coatings have a higher thermal expansion coefficient, higher hardness and toughness, and more resistance to corrosion, abrasion and erosion [2].

Polymer composite has presented itself as advanced materials to satisfy the demand for the development of advanced engineered materials for various applications [3].

Due to their thermal stability and other characteristics like strength, stiffness, and durability, polymers have a limited potential to take on unique shapes. Most thermoplastics degrade at comparatively low temperatures. Due to this behavior, most thermoplastic non-reinforced polymers cannot be utilized in high-temperature tribological applications. Numerous techniques are offered to enhance the tribological behavior of the polymers due to the poor corrosion rate of most basic polymers [4].

Because of the importance of these materials in applications including reducing drag in microfluidic devices, self-cleaning surfaces, and preventing consumption and fouling, the development of multifunctional polymer coatings has recently received a lot of attention[5].

Although the use of fillers in plastics industry has been known for several decades, there is still an enormous interest in all the fields of the development of composite materials with enhanced properties. Mineral fillers are added to the polymers in commercial production primarily for reasons related to cost reduction and properties improvement, improving the existing materials, and developing new materials [6].

Over the past several years, polymer nanocomposites have attracted much attention because of good optimal outcomes, high transparency, low cost, low density, ease of manufacturing, flexibility, low thermal expansion, and ease of handling [7].

Polymer blends and composites have become a central part of polymer science and engineering because people could make composites that have properties substantially unattainable with homo-polymers. Such properties include greater toughness, higher strength, better ductility, better absorption properties [8].

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In recent years, the use PMMA polymer as a substrate is employed for the formation of microchannel structures[9].

Enhancements in utilizing Poly (methyl methacrylate, or PMMA) have facilitated the realization of a diverse array of nanotechnology applications[10]. The recent advancements in the synthesis, modification, and utilization of PMMA have been significantly impacted by our expanding comprehension of its inherent features [11].

However, it is necessary to summarize these changes for easier access and greater comprehension in the form of an article. Presented here emphasizes PMMA's essential physical characteristics and includes experimental evidence of its fundamental chemistry, including grafting, combustion, hydrolysis, solubility thermal breakdown, and amine reactions, in addition to the current improvements in the use of PMMA in optical, photovoltaic, and medicinal applications [12].

As a graphene derivative, graphene oxide (GO) is an oxidized form of graphene having oxygen-containing functional groups connected to its edges and surface, such as epoxy, hydroxyl, and carbonyl [13]. Graphene oxide (GO) emerged as a new carbon-based nanomaterial known for its complex carbon structure and strength properties. [14]

This exhaustive analysis delves into the chemical features and characteristics of graphene oxide. Special attention is dedicated to the manufacturing process of graphene oxide and its structural characteristics. This review shall benefit synthetic chemists interested in this emerging domain of materials science and researchers exploring graphene applications. The comprehensive examination of the chemistry of graphene oxide within this review shall aid in comprehending the extent and limitations of existing methodologies employed in utilizing this substance. Graphene oxide (GO), denoted as  $C_{140}H_{42}O_{20}$ , is a unique material consisting of a solitary monomolecular layer of graphite featuring various oxygen-containing functionalities, including hydroxyl, carboxyl, carbonyl, and epoxide groups [15].

Nanoparticles that may be dispersed on nanoscale would outcome in extremely great interaction between these particles and the matrix resin[16].

Tribology is the science and technologies of surfaces of materials concerning one another, including friction, lubrication, and wear. Tribology is a branch of science that uses operational analysis to solve issues with significant commercial implications, including the dependability, maintenance, and wear of technological equipment ranging from home appliances to spacecraft [17].

Composite materials consist of a synergistic amalgamation of two or more constituent materials, wherein the primary component is the matrix. In contrast, the remaining components are denoted as additives or strengthened materials. The materials exhibit distinct characteristics and maintain their individuality at a macroscopic level within the ultimate structure [18].

It is occasionally necessary to have a rough surface to obtain an effective transfer suitable for a particular medium. As a result of the erosion and rubbing of the two surfaces, friction processes frequently leave behind residues causing a friction layer to form, which allows for a qualitative assessment and a description of the surface's slip performance. Both polymers and compounds may be

studied individually in terms of these tribological processes. As illustrated in the formula below, the coefficient of friction (COF) may be defined as the proportion between the average load (FN) and the frictional force (Ff).The frictional behavior is influenced by the application of shear forces and the failure of the material in the vicinity of the contact area between the two surfaces during sliding [19].

In dry slip conditions, wear can be described as a phenomenon occurring at the interfaces of the interacting bodies[20]. The technological revolution has given rise to cutting-edge engineering products encompassing high-speed sliding, rolling, or small-dimensional geometric shapes designed to withstand harsh and challenging environments. These products' successful development and utilization in various fields necessitate effectively mitigating corrosion challenges, which can be achieved by leveraging insights from prior experiences and comprehensive studies conducted in the past and present [21].

The tribological performance of thermoplastic polymers is enhanced by including fillers or fibers, which strengthen the surface. Polymeric materials are routinely filled with fillers, including particles, to increase processability and mechanical compound characteristics while minimizing material costs. The filler behavior in the compound was impacted by the distribution of particle sizes, the surface area, the shape, and surface chemistry [22].

## 2. Experimental part

### 2.1. Utilized Materials.

Poly (methyl methacrylate) (PMMA), commonly called acrylic or acrylic glass, is a thermoplastic polymer with a melting point of 160 °C. It possesses a refractive index of 1.4905 nm. On the other hand, modified Graphene oxide (MGO) and Graphene oxide (GO)  $C_{140}H_{42}O_{20}$  is an exceptional material that can be perceived as a solitary monomolecular layer of graphite. It exhibits diverse oxygen-containing functionalities, including hydroxyl, carboxyl, carbonyl, and epoxide. (Trimethoxy sily) propyl methacrylate (TMSPMA) is a commercially available hydrophobic monomer widely utilized in the materials engineering field in Iraq.

### 2.2. Specimen Preparation

The technique utilized for coating is the "solution-casting technique" [23]. The procedure of preparing PMMA nanocomposites consisted of PMMA with the GO and PMMA with MGO. In order to prepare the nanocomposite, the nano GO powder was dried at 100 °C for 2 hours under vacuum. The filler was weighted in the required proportions and PMMA

nanocomposite with (0.25, 0.5 and 1) wt. % GO, and(0.25, 0.5 and 1) wt. % GO modified. The procedure for preparing PMMA nanocomposites consisting of the polymeric materials were carefully washed with alcohol to remove oils, dust, grease or any surface contaminants.

The material is in the form of particles. They were then weighed according to the appropriate proportions for mixing. Preparing PMMA Nano composite with PMMA particles weighing 10 g were dissolved in THF solvent with

a volume of 5 ml and stirred for 4 hours to make the composite material. The GO solution was prepared by dissolving the GO in 5 ml of THF as the solvent.

A solution was then placed in a sonication dispersion device for 30 minutes, and after that, the solution was included. An hour was then spent mixing the polymeric solution, then the solution was poured into the polymeric mold. The modified graphene oxide samples were made using the same procedure. The process was repeated for each sample, and they were ready to evaluate the microstructure, tribological, and mechanical tests.

**Table 1.** Polymeric composites compounds

N	Sample Code	Sample Composition
1	Pure PMMA	PMMA Only
2	PMMA\GO 0.25	Pure PMMA\graphene oxide 0.25 wt%
3	PMMA\GO 0.5	Pure PMMA\graphene oxide 0.5 wt%
4	PMM\GO 1	Pure PMMA\graphene oxide 1 wt%
5	PMMA\MGO 0.25	Pure PMMA\graphene oxide Modified 0.25 wt%
6	PMMA\MGO 0.5	Pure PMMA\graphene oxide Modified 0.5 wt%
7	PMMA\MGO 1	Pure PMMA\graphene oxide Modified 1 wt%

### 2.3. TESTS

#### 2.3.1. Differential Scanning Calorimetry (DSC) test

The test was done using a SHIMADZ-4 DSC-60 equipment in accordance with ASTM D3418-03. The samples of pure materials (PMMA) and PMMA nano graphene oxide in powder form were analysed under nitrogen gas and a heating rate of 10 °C / min between 25 and 350 °C.

#### 2.3.2. Pin-on-disk

The dry friction and wear characteristics of Pure PMMA and PMMA Nanocomposite with GO and MGO were investigated utilizing the Pin-on-disk technique. In pin-shaped fixtures, an aluminum ball was utilized; therefore, it

is reasonable to infer that there is just sliding friction between the parts. The usual load, slip speed, beginning temperature of the test medium, and slip distance between damaged couplings all impact the loading situation in the pin-to-disk test.

#### 2.3.3. Hardness TEST

Vickers hardness test equipment was utilized to measure hardness. Its indenter is a diamond pyramid with a square base. It was decided upon the weight of the load (25 grams) and the duration (10 seconds) for application.

#### 2.3.4. Scratch Test

The scratch hardness test measures the resistance of a material to scratches and abrasion caused by sharp object contact. The ISO 1518 standard is used to describe a method for determining how resistant a single coating or multi-coat system of paint, varnish, or a similar product to penetration is by the scratching with, a stylus loaded to a certain load.

A method to determine how resistant a single coating to penetrate is  $H_{sp} = \frac{4qP}{\pi w^2}$

$H_{sp}$  is considered the scratch of hardness,  $W$  stands for the measured scratch width,  $P$  represents the applied normal load, and  $q$  represents a factor ranging from 1 for elastic materials to 2 for plastic materials ( $q$  is considered to have a mean value of 1.5). Due to the fact that most polymers are naturally viscoelastic or viscoelastic in this study

#### 2.3.5. Ultraviolet-visible spectrophotometer Test

UV-Visible – CECIL 2700 computerized spectrophotometer used to assess the sample's optical characteristics. The sample is positioned in a certain location on the UV/VIS instrument. depicts the operating principle of a double beam spectrophotometer, which employs two beams of light: a reference beam and a beam that passes through the sample as a sampling beam.

#### 2.3.6. Scanning Electron Microscope SEM test

The surface of the sample is imaged by scanning electron microscopy (SEM) by scanning it with a high-intensity electron beam in a raster scanning pattern. These electrons interact with atoms of the sample surface to produce signals that provide details of the surface topography. Analytical scanning electron microscopy (SEM) model (JEOL 6400 F) was utilized to examine the morphology of films according to (ASTM 986-04).



**Figure 1.** Samples of Polymeric composites

**3. Results and discussion**

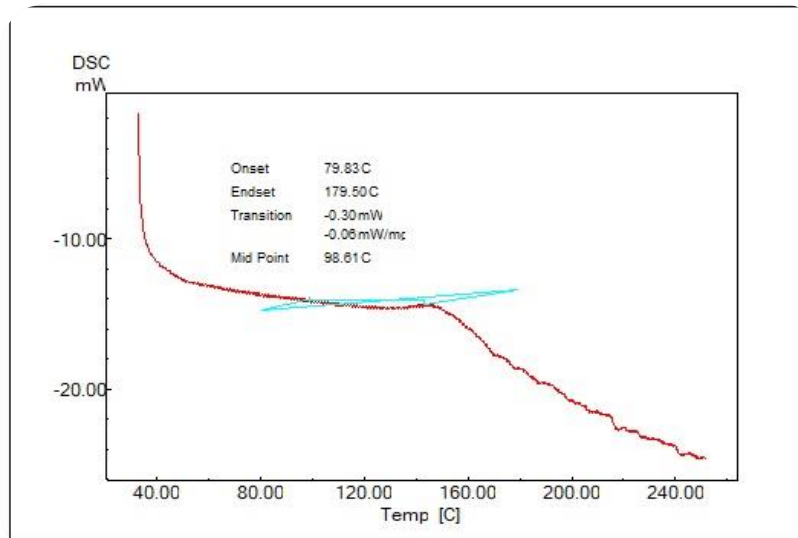
*3.1. DSC Test*

DSC analysis of pure PMMA which used to determine PMMA and PMMA nano-composites glass transition temperatures. The results showed that Neat PMMA has a  $T_g$  of 99 °C. Figure 3 is PMMA containing 0.25 wt% GO nanoparticles had a glass transition temperature ( $T_g$ ) that was approximately 10 °C higher than that of pure PMMA. The  $T_g$  values for PMMA containing 1 wt% GO and 1 wt% MGO. were approximately 18 °C and 19 °C higher, respectively. Because of the large specific surface area of nanoparticles and their homogeneous dispersion within the matrix, these particles are able to effectively act as nucleating agents[24], as shown in Figures4 and 5 Additionally, increasing in  $T_g$  can be attributed to the nanoparticle's occupation of a space in the PMMA lattice, which in turn restricts the mobility of chain diffusion.

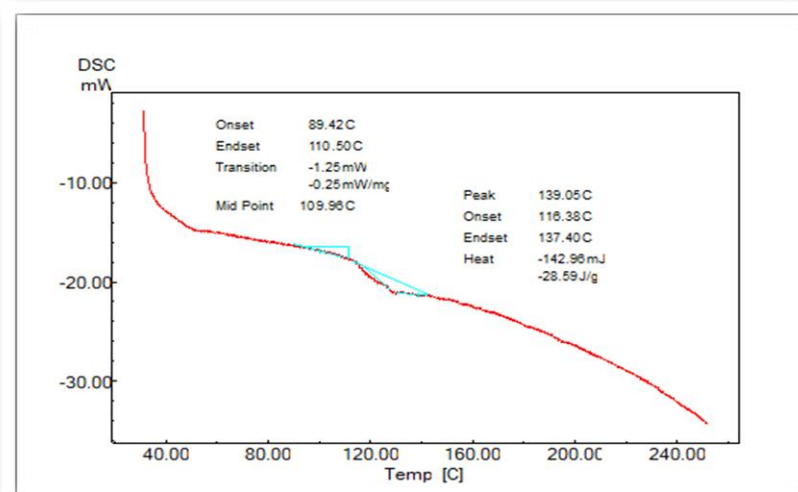
So it is clear, that  $T_g$  values increased linearly from 99 C° (for PMMA up to 117 C° (for sample with 1 wt% MGO.) 19% . This increment in  $T_g$  gives an indicator about the improvement of the mechanical properties of the prepared samples as well as the thermal stability. When Graphene Oxide amounts increased within the composite structure, the steric hindrance increased, so the polymeric chain restricted and cannot be sliding above each other, which leads to increase  $T_g$  and this agrees with[25].

**Table 2.**  $T_g$  for PMMA and it's composites

Sample	$T_g$
PMMA	98.61 °C
PMMA\GO 0.25 wt%	109.96 °C
PMMA\GO 1 wt%	116.53 °C
PMMA\MGO 1 wt%	117.58 °C



**Figure 2.** DSC curve For PMMA



**Figure 3.** DSC curve for PMMA\GO 0.25 wt%

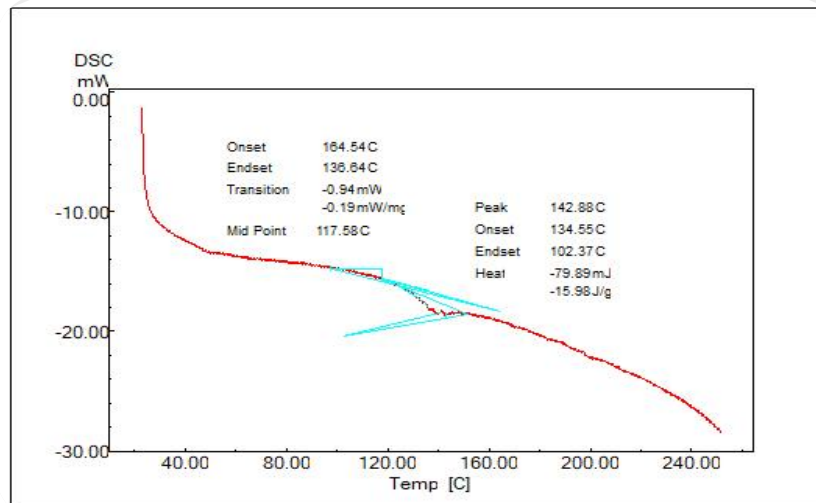


Figure 4. DSC Curve For PMMA\GO 1 Wt%

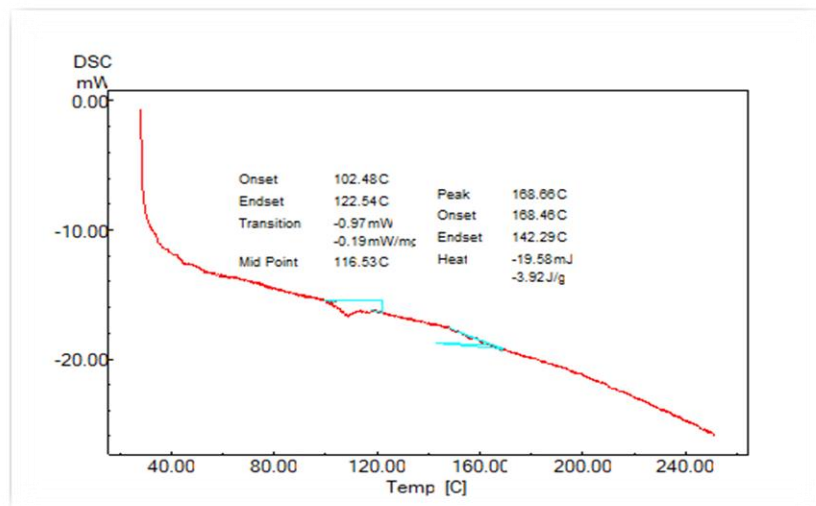


Figure 5. DSC Curve For PMMA\MGO1 Wt%

### 3.2. Coefficient of Friction and Wear result

According to the findings, the friction coefficient reduced in a linear fashion when the weight percentage of GO increased. Specifically, the coefficient of friction changed from 0.78 for pure PMMA to 0.68 for PMMA that had been reinforced with GO 1 wt %, as shown in Figure 6. This might be attributed to cleavage of graphene oxide layers which behave as a solid lubricant. As shown in Figure (6) Addition of MGO can cause a significant reduction in friction coefficient of (PMMA/MGO nanocomposite, which was decreased (from 0.78 to 0.67) and the coefficient of friction decreases as the MGO content increases [26].

The wear rate losses of PMMA/GO and PMMA/MGO Nanocomposite decrease as the GO,MGO content increases, and this behavior is related to the role of GO and MGO as a solid lubricant. GO and MGO may decrease the interfacial shear stress at the contact zone. Figure 7 showed (0.25%, 0.50%, and 1%) GO and MGO PMMA. GO can enhance the wear resistance when sliding. GO nanoparticles

worked as a solid lubricant on the samples surface during testing, and their resistance to rubbing during sliding decreased wear volume loss. The wear rate decreased by 58% for PMMA\GO 1 wt % and decreased by 69% for PMMA\MGO 1 wt% as compared for pure PMMA[27].

### 3.3. Hardness Test

Material hardness is defined as the resistance of material against surface deformation caused by external load. The Vickers hardness test for PMMA nanocomposite is shown in Figure 8 The hardness of the PMMA increases with increasing nanoparticles content addition. The microhardness measured values as the GO content changed, Density increased as the GO content increased, with an increase of micro hardness from 11 to 18.4 HV. Figure (8) showed the hardness of the pure PMMA and PMMA reinforced with GO and MGO. The increase in GO and MGO content caused to increase of hardness value[28]. The hardness value increased by 96% for PMMA\GO 1 wt% and 100% for PMMA\MGO 1wt%.

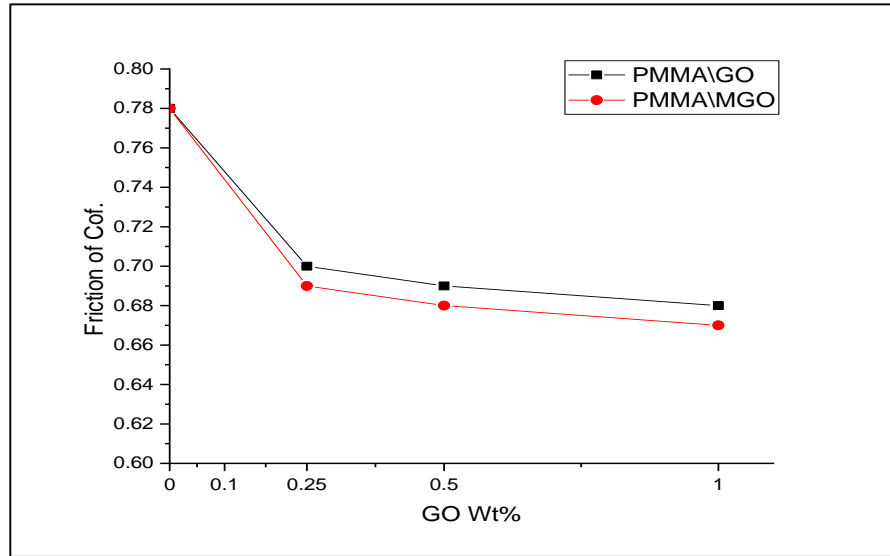


Figure 6. Friction of Coefficient. For PMMA\GO And PMMA\MGO

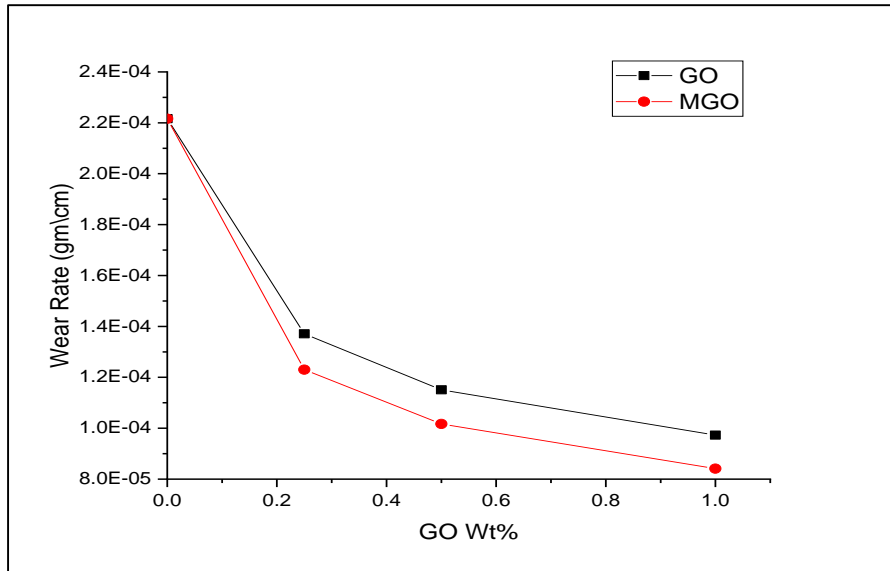


Figure 7. Wear rate for PMMA\GO and PMMA\MGO wt %

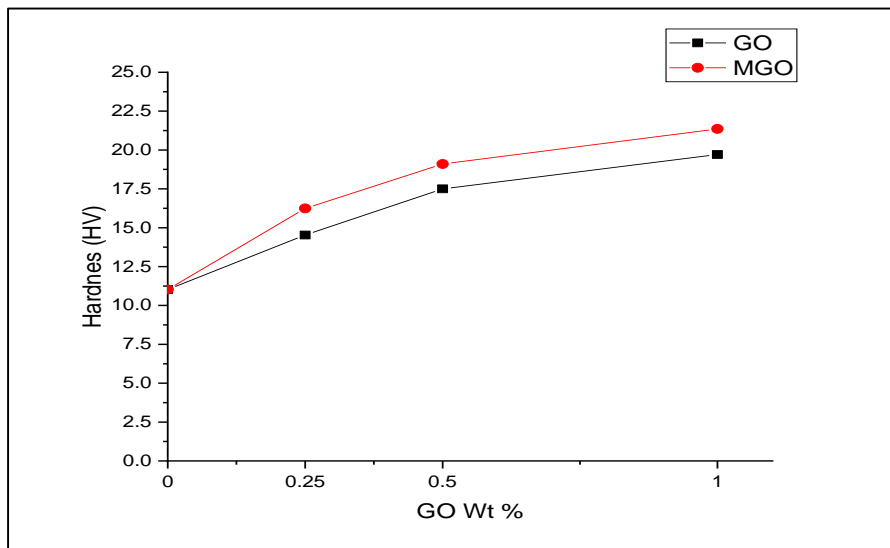


Figure 8. Micro Hardness test for PMMA\GO And PMMA\MGO wt%

3.4. Scratch test

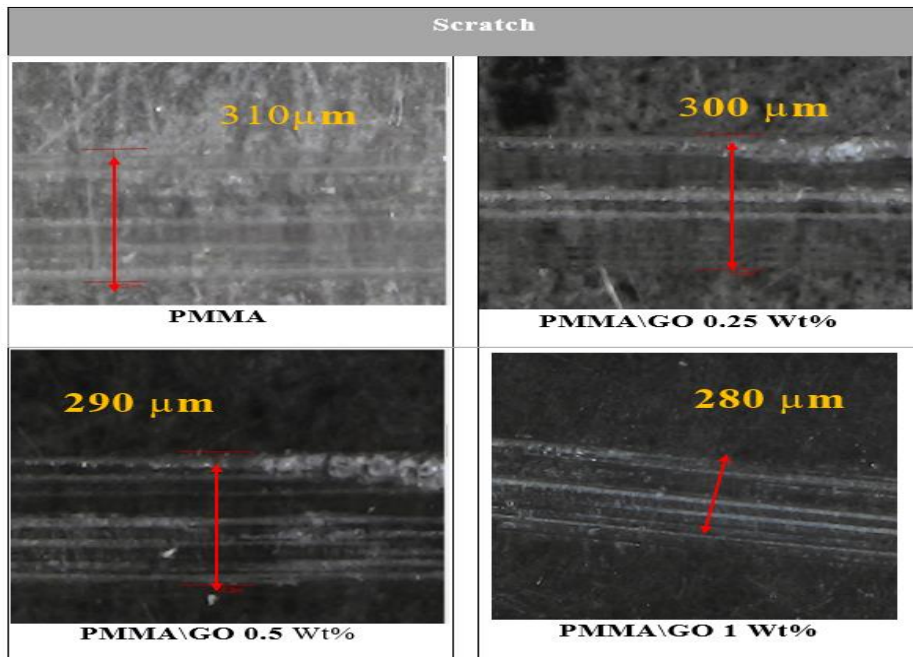
Addition of GO and MGO to PMMA can enhance scratch hardness to 23 % and 32 %, respectively under 0.5 kg probe load compared to pure PMMA. Materials with suitable value of hardness, elastic modulus have high scratch hardness as shown in Table 4.3. It seems that with increasing GO and MGO weight percentage the plastic deformation was reduced.

PMMA reinforced with GO and MGO showed a scratch resistance more than pure PMMA. Adding silane coupling agent can surface adjustments for GO improvement enhances dispersibility and interfacial interactions between the nanofiller and the matrix due to efficient load transfer using silane, which was responsible for the improvement of

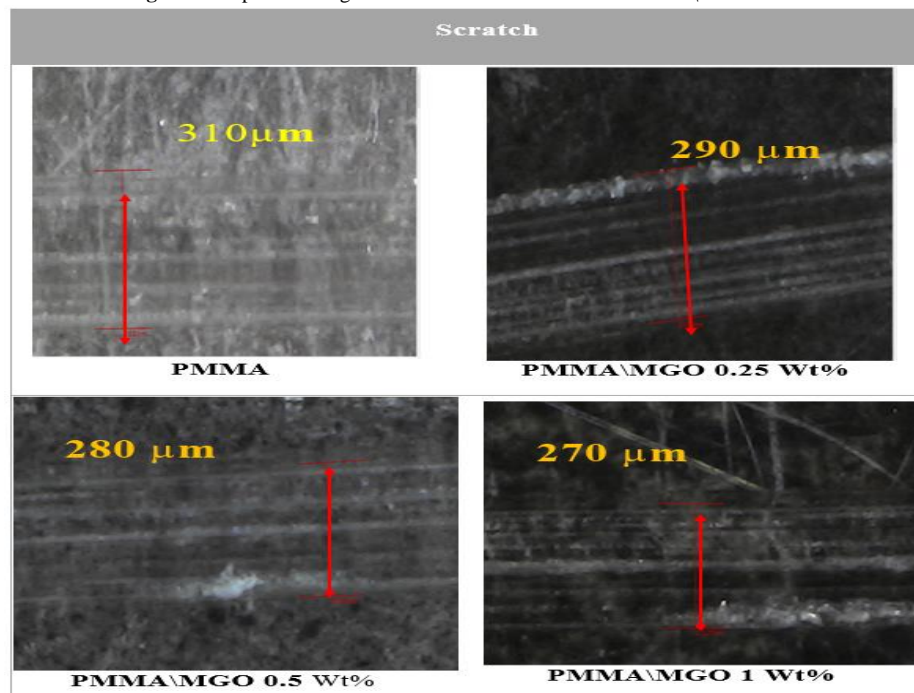
several mechanical properties, and this agrees with increase in hardness and corresponding enhancement on scratch resistance[29].

**Table 3.** Scratch hardness for PMMA and its composite (PMMA, PMMA\GO, PMMA\MGO)

Sample	Scratch hardness value (MPa)
Pure PMMA	0.0119
PMMA\GO 0.25 wt%	0.0127
PMMA\GO 0.5 wt%	0.0136
PMMA\GO 1 wt%	0.0146
PMMA\MGO 0.25 wt%	0.0136
PMMA\MGO 0.5 wt%	0.0146
PMMA\MGO 1 wt%	0.0157



**Figure 9.** Optical images for Scratch hardness for PMMA\GO



**Figure 10.** Optical images for Scratch hardness for PMMA\MGO



3.5. UV Spectroscopy Results

Figure (11) depicts the absorption characteristics of the produced specimens within the ultraviolet (UV) electromagnetic spectrum regions. Within the UV region, the absorption positively correlated with the augmentation of the graphene oxide amount, which implies that incorporating graphene oxide induced alterations in the electronic energy levels in the composite polymeric structure. These modifications enable the structures to absorb and disperse detrimental ultraviolet (UV) rays as minimal, innocuous thermal energy. This benefit is commendable, as it affirms that composite films can mitigate the hazards associated with UV degradation and sustain operational longevity.

An increase in absorption is observed with the increase in graphene oxide concentrations.

Figure (12) illustrates a reduction in Transmittance as the concentration of graphene oxide increases. The UV-V spectra analysis reveals that the PMMA/GO nanocomposite exhibits absorption within the range of approximately 250 nm to 400 nm, signifying its ability to attenuate UV radiation effectively. Therefore, GO functions as a barrier that inhibits the transmission of UV radiation and provides UV protection. With an increase in the weight percentage (wt%) of graphene oxide (GO) nanoflakes, there was a notable reduction in Transmittance within the ultraviolet (UV) spectrum. At the same time, the transparency within the visible range remained unaffected. This observation was made through the analysis of digital images of the films. The transparency reduced from 92 percent for the PMMA polymer, which is highly transparent, to 75 percent for the 0.1 wt% graphene oxide-reinforced polymer, which is acceptable within the visibility range[30].

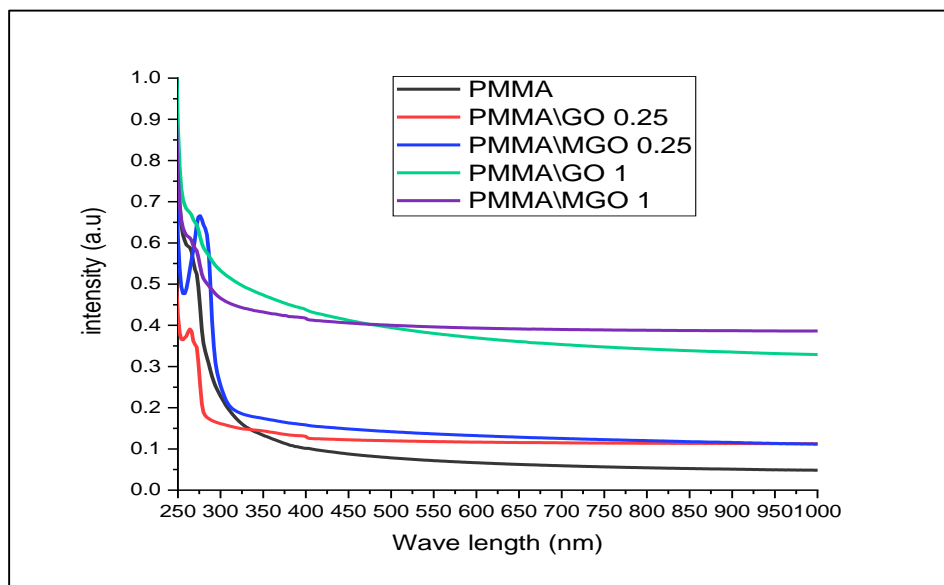


Figure 11. UV-absorbance of PMMA, PMMA\GO 0.25 %, PMMA\GO 1 % samples.

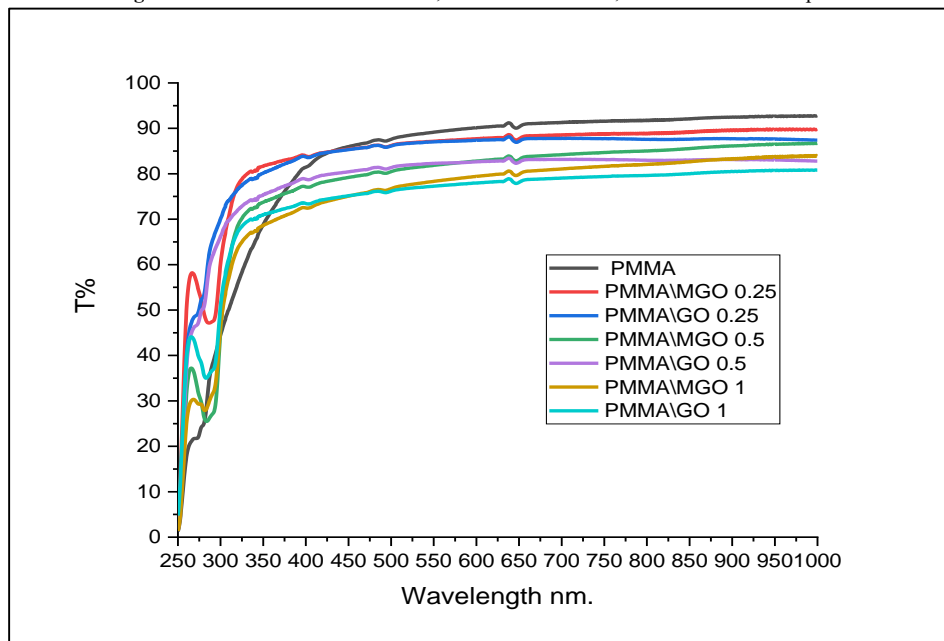


Figure 12. UV- Transmittance of PMMA, PMMA\GO 0.25 %, PMMA\GO 0.5 %, PMMA\GO 1% specimens

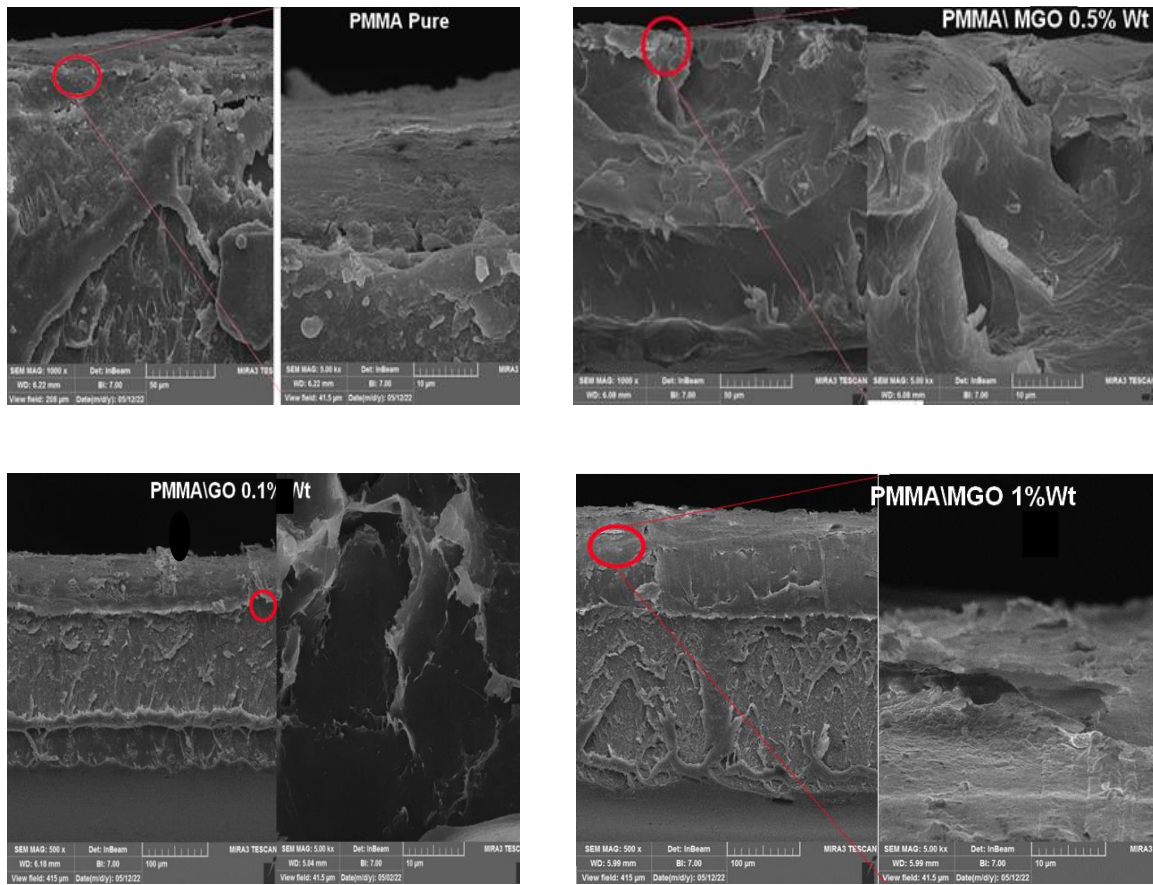


### 3.6. Field Emission Scan Electrons Microscopy Results

Scanning electron microscope (SEM) is used to show the morphology and nanoparticle distribution in the polymer matrix (Figure13), it is clear that GO nanoparticles are well dispersed through the PMMA matrix and there is a little agglomeration of the nanoparticles in the structure of the polymer. It can be observed also, in low content GO (0.25 and 0.5%) particles are dispersed homogeneously inside the PMMA matrix with a very few agglomerates. On the other hand, when the filler content increased (1%), agglomeration increased with a reasonable proportion of particles distributed at the nanoscale. As it was observed during sample fabrication, the matrix viscosity significantly

increased as nanoparticle concentration increased. Further increases in GO produce an increase in the brittleness of the PMMA matrix[31].

Additionally, low content MGO (0.5 and 1%) particles are seen to be uniformly dispersed within the PMMA matrix with very few agglomerates. On the other hand, agglomeration increased with a reasonable proportion of particles distributed at the nanoscale as the filler content increased (1%) in the sample. The matrix viscosity significantly increased as the nanoparticle concentration increased, as was seen during sample fabrication. The brittleness of the PMMA matrix increases as GO continues to rise[32].



**Figure 13.** SEM Image for pure PMMA and its composite (PMMA, PMMA\MGO 0.5,PMMA\GO 1 , PMMA\MGO 1

#### 4. Conclusions

In this work, the PMMA polymer was reinforced by adding graphene oxide fillers to enhance the tribological behavior of PMMA utilizing the solution mixing technique.

DSC testing, shows a rise in  $T_g$  with increasing GO and MGO content. DSC tests are suggestive of the fact that the composite (PMMA/GO, PMMA/MGO) are good compatible composite and the result showed that there is improvement in  $T_g$  with increasing of GO and MGO content. Scratch test shows improvement in scratch hardness with increasing of GO and MGO and with addition of PMMA/MGO\ 1 show increasing by 32% in scratch hardness compering with pure PMMA. The SEM micrographs provide evidence of significant alterations in surface morphology upon the introduction of GO and MGO into the PMMA polymer. These changes suggest interaction and interface formation between the GO and MGO and PMMA matrices, likely resulting from cross-linking, wherein the mechanical characteristics of the nanocomposite exhibit enhancement upon the incorporation of GO. In contrast, the tribological characteristics demonstrate improvement upon the inclusion of GO. By performing a micro hardness from 11 to 18.4 HV showed the hardness of the pure PMMA and PMMA reinforced with GO and MGO. the increase in GO and MGO content caused to increase of hardness value. The hardness value increased by 96% for PMMA/GO 1 wt% and 100% for PMMA/MGO 1wt%. By examining the UV, we notice that adding graphene oxide increased the UV absorption and reduced the transparency. However, it remained within the transparent range because the percentages utilized for graphene oxide were relatively few.

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